

Biochemical Removal of HAP Precursors From Coal

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Introduction

This project addresses DOE's interest in advanced concepts for controlling emissions of air toxics from coal-fired utility boilers. We are determining the feasibility of developing a biochemical process for the precombustion removal of substantial percentages of 13 inorganic hazardous air pollutant (HAP) precursors from coal. These HAP precursors are Sb, As, Be, Cd, Cr, Cl, Co, F, Pb, Hg, Mn, Ni, and Se. Although rapid physical coal cleaning is done routinely in preparation plants, biochemical processes for removal of HAP precursors from coal potentially offer advantages of deeper cleaning, more specificity, and less coal loss. Compared to chemical processes for coal cleaning, biochemical processes potentially offer lower costs and milder process conditions.

Pyrite oxidizing bacteria, most notably *Thiobacillus ferrooxidans*, are being evaluated in this project for their ability to remove HAP precursors from U.S. coals. These bacteria convert pyrite and other metal sulfides to soluble metal sulfates. There is disagreement over the significance of mechanisms of this reaction. The organisms enzymatically oxidize the sulfur of pyrite with oxygen to form sulfate. The organisms also enzymatically oxidize ferrous iron in solution with oxygen to ferric iron. The ferric ions oxidize pyrite and other metal sulfides to sulfates, via the so called "indirect mechanism". The reaction of ferric ions with pyrite does not require oxygen; the oxygen in water is incorporated into sulfate: $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$. The majority of published evidence suggests that the major role of microorganisms in the oxidation of pyrite is via the indirect mechanism--to regenerate ferric ions from the ferrous ions formed in the above reaction.

The metabolism of pyrite oxidizing bacteria makes them good candidates for removing HAP precursors from coal, since many of the HAP precursors in coal are believed to occur as substitutions for iron in the pyrite lattice, as distinct sulfides, or in minerals susceptible to dissolution by acidic, oxidizing conditions.

Reliable quantitation of HAP precursors in coal is a challenge. Therefore, a key component of any test program to evaluate removal of HAP precursors from coal is the analytical quality control program. The analytical program in this project has included 1) use of NIST reference coal certified for trace element content to validate the analytical methods, 2) analysis of blanks carried through all digestions to verify the absence contamination, 3)

determination of mass balances for each HAP precursor element in each experiment, 4) interlaboratory comparison of analytical results in special cases (Hg).

Objective

The overall goal of the project is to determine the feasibility of developing a biochemical process for the removal of 13 HAP precursors and sulfur from coal. Specific objectives in phase 1 of this project are 1) determine the correlation between microbiological pyrite removal and HAP precursor removal from four U.S. coals, 2) test the feasibility in column tests of removing HAP precursors and pyrite by leaching with solutions containing Fe(III), maintained by iron oxidizing bacteria, and 3) test the performance of the Idaho National Engineering Laboratory's (INEL) slurry column reactor in removing HAP precursors from Pittsburgh coal.

Approach

The technical approach to large scale biochemical removal of HAP precursors from coal most likely would involve one of two routes: 1) leaching of relatively coarse coal (particle sizes of 1/2" to 2") in heaps or vats, or 2) leaching/physical separation with fine coal (ca. 60 mesh) in a slurry column reactor. Although biooxidation of pyrite and other metal sulfides in heaps is increasingly practiced in copper and gold mining, there are limits to the applicability of this technology to coal cleaning. Most noteworthy, a key recent development is the use of forced air ventilation of heaps to maximize biooxidation of sulfides and iron on ore surfaces and in interstitial leach solutions. This ventilation maximizes biooxidative reactions, with the result that heaps can get hot. Temperatures in excess of 60°C have been measured in heaps of ores containing only 1 to 2% sulfide sulfur, comparable to the pyritic sulfur content of many coals. Coal combustion in large heaps is a danger under such conditions. Indeed, a pile of Pittsburgh coal weighing only 20 tons exhibited significant heating (up to 42°C in a study by Hyman and Hammack) before water was added to quench the system.

The current study proposed the novel approach of using ferric ions to remove pyritic sulfur and HAP precursors from coal. The ferrous iron formed would be reoxidized by iron oxidizing bacteria with oxygen to ferric ions in a rotating biological contactor (RBC) prior to reapplication to coal heaps. The RBC is an efficient and inexpensive means to reoxidize ferrous iron, and the danger of coal combustion would be averted.

The approach of the phase 1 test work was to use shake flask tests and columns to determine the extent that pyrite oxidizing bacteria remove HAP precursors from coals and the correlation of pyrite removal with the removal of HAP precursors. Short term flask tests of pyrite oxidation and column tests were conducted to determine if ferric ion-based leaching could remove pyrite and HAP precursors from coal at reasonable rates. The removal of HAP precursors from coal was also tested in the INEL slurry column reactor. The slurry column reactor was developed with DOE support and is an advanced concept for

combined microbiological and physical cleaning of finely ground coal. Large particles of pyrite and associated HAP precursors are separated from coal by physical removal and micropyrith is removed microbiologically.

During phase 1, preliminary process design work also led to the conclusion that continuous vat leaching offers advantages over a heap leaching approach to removing HAP precursors and pyrite from coarse coal (1/2"). Most notably, vat leaching kinetics would be faster than heaps due to improved contact of leach solutions with coal, and a continuous vat process would be more controllable.

Procedures

Initial tests were done in shake flasks with slurries of finely ground coal (minus 100 mesh) in dilute mineral salts medium at a pH of about 2.0. Flasks were inoculated with mixed cultures of pyrite oxidizing bacteria. The progress of microbial pyrite oxidation was monitored by analysis of solution pH, redox potential, and concentration of dissolved ferrous iron, total iron, and sulfate. Some flasks remained as uninoculated controls and received a solution of thymol in methanol to inhibit microbial activity.

Leach column tests were done with 28 x 100 mesh coal loaded into 2 in. x 1.5 ft. plastic columns. Leach solution was collected in a reservoir in which a small RBC unit was operated. Leach solution was recycled to the columns.

The concentration of HAP precursors in starting coal, bioprocessed coal, and in leach solutions was determined in both shake flask and column tests and analytical mass balances for all 13 HAP precursors were determined. Starting coal and product coal received an ultimate, short proximate, and forms of sulfur analysis

Short term (24 hr) tests of pyrite oxidation in Pittsburgh coal were also conducted. The coal (28 x 100 mesh) was shaken in a 25% w/v slurry at room temperature in a biogenic, oxidizing leach solution at pH 1.9 containing 16.6 g/l of ferric iron. The production of ferrous iron was measured to determine the rate of pyrite oxidation by ferric ions. The pH and redox potential were measured also.

The INEL slurry column reactor was operated with 60 mesh Pittsburgh coal. The reactor combines microbiological and physical coal cleaning processes. Briefly, the process consists of two aerated reactors, the rougher-propagator and the clean coal reactor. Coal is added to the clean coal reactor and aerated for a short period of time with leach solution from a previous batch of coal. Aeration is interrupted, and the heavier particles are allowed to settle prior to their removal to the rougher-propagator reactor. The heavier particles contain larger pieces of pyrite which are more efficiently removed from coal by gravity than by microbial oxidation. Aeration is resumed in both reactors. Microbial oxidation of micropyrith occurs in the clean coal reactor (typically for 2 to 5 days, depending on the cycle time), and then the clean coal is washed and removed. Microbial pyrite oxidation

occurs also in the rougher-propagator reactor. The function of the rougher-propagator reactor is simply to grow more pyrite oxidizing bacteria. The solids from the rougher-propagator are then removed to waste. The leach solution containing pyrite oxidizing bacteria from the rougher-propagator reactor is then mixed with a fresh batch of coal.

Results

Shake Flask Tests. The shake flask tests with finely ground coal showed pyrite oxidizing bacteria removed substantial percentages (30 to 70%) of HAP precursors As, Co, Cd, Mn, and Ni from Pittsburgh No. 8, Indiana No. 5 (preparation plant cleaned) and Kentucky No. 9 coals. Lesser amounts (5 to 20%) of Se, F, and Be were also removed. Results were similar with Rosebud (Montana subbituminous) coal, except that Be was significantly mobilized and As was not. Mn, Cd, Co and Ni were generally dissolved more rapidly than pyrite. Mn and Co were also significantly dissolved in the control solutions, indicating they were bound in acid labile forms.

Column Tests. Column tests with ferric ion-RBC leaching of Pittsburgh, Indiana, and Kentucky coals showed significant dissolution of the same HAP precursors as in shake flask tests (As, Cd, Co, Mn, Ni). About 50% of the pyritic sulfur was removed in one month from Pittsburgh and Indiana coals and in two months from Kentucky coal. In separate tests, leach solutions were spiked with high concentrations of ferric ions to more closely simulate properties of the expected process solutions. The iron was maintained in the ferric state microbiologically, and HAP precursors were removed more rapidly than in the tests conducted at lower ferric ion concentrations. In both shake flask and column tests, mass balances for the 13 HAP precursors were almost always within a range of 80 to 120%.

The pyrite oxidation kinetics observed in the column tests were not representative of optimized conditions. In subsequent short term tests of pyrite oxidation (described below) the maintenance of high redox potential, not simply the presence of ferric ions, was identified as the key to high rates of pyrite and associated HAP precursor removal. Though iron oxidizing bacteria were able to maintain a relatively high ratio of ferric to ferrous iron in leach solutions, the columns were not operated under conditions (i.e., solution flow rates) which maximized redox potential in solutions exiting the columns.

Rate of Pyrite Oxidation by Ferric Ions. Short term tests of pyrite removal from Pittsburgh coal indicated that maintenance of high redox potentials (>700 mV s.h.e.) were required for the most rapid oxidation of pyritic sulfur in coal. A fairly small ratio of ferrous iron to total iron (0.1 to 0.2) was sufficient to significantly depress the redox potential and slow the rate of pyrite oxidation considerably. For example, pyrite oxidation rates of 13% per day were measured early in the test during the time interval in which the redox potential decreased from 849 to 744 mV. The daily oxidation rate declined as the redox potential declined, to a rate of 2.7% in the final time interval in which the redox potential declined from 700 to 682 mV. However, even at the end of the final interval, the concentration of Fe^{3+} was still 14.5 g/l compared to an initial concentration of 16.6 g/l Fe^{3+} . The implication

of these results is that rapid recycling of leach solutions to the RBC will be necessary to maintain a high redox potential in solutions exiting the heap or vat reactor.

Tests of Hg Removal. Additional test work was done following the results of shake flask and column tests which showed Hg was not mobilized by pyrite oxidizing bacteria. Following bioleaching of a portion of the pyrite, 70% of the Hg could be removed from Pittsburgh coal by 6N HCl, compared to 30% removal of Hg by HCl from raw coal. These results suggest that microbial pyrite oxidation exposes Hg otherwise hidden inside pyrite crystals. Thermophilic sulfide-oxidizing microorganisms were tested for their ability to remove Hg from coal and from HgS. No evidence was obtained for Hg solubilization. However, the Hg content of clay fines suspended above biotreated coal was 3 times higher than above control coal, suggesting that microorganisms may enhance the physical separation of Hg from coal. The test work indicates that although microorganisms do not solubilize Hg, they may expose Hg to extraction or render it more removable from coal by subsequent physical separation.

Slurry Column Reactor Tests. Preliminary data from the slurry column reactor indicated removal of 40 to 70% of the HAP precursors from Pittsburgh coal with the exception of Cl (20% removal), F (30%), and Be (20%). Sb was not detectable. About half of the pyritic sulfur was removed also. The slurry column test work was consistent with findings of the shake flask and column tests in that As, Co, Cd, Ni, and Mn were significantly leached into solution in the biochemical portion of the reactor. Cr, Se, Be, Pb, Cl and F were also leached into solution. Hg was not detected in solution. However, significant Hg was removed in the physical cleaning component of the system: Hg in feed coal was 0.12 ug/g, and was reduced to 0.054 ug/g in the product coal. Waste coal contained 0.24 ug/g Hg. The results with thermophilic bacteria described above and recent findings that Hg is difficult to remove from coal by physical cleaning suggest that microorganisms might have improved the separation of Hg from coal in the physical cleaning part of the process. However, additional testing is required to prove this assumption. Se, another key HAP precursor, was also removed significantly (50%) from coal by both biochemical and physical processes in the slurry column reactor.

Mass balances were calculated for the slurry column process by analysis of feed coal, product coal, waste coal, and in wastewater liquids and wastewater solids after neutralization of effluents. The preliminary results indicated mass balances for all HAP precursors were in the range of 75 to 100%.

Process Design. Two process design configurations for the Phase 2 pilot plant were completed through the conceptual stage for microbial removal of HAP precursors in both a "heap leaching process" and a "continuous vat leaching process". Both process pilots will be tested during Phase 2, as the contribution of particle size to the overall kinetics of the two processes have economic importance that must be revealed during pilot testing for further process development and scale-up. Most power plants require coal to be larger than 1/4" in the storage yard prior to entry into the plant feed system. A heap leach process

could have an effective top size of about 2" while a continuous leach process would have an effective top size of about 1/2".

Application/Benefits

The benefits of a biochemical process for removal of HAP precursors and pyrite from coal will be realized only if the biochemical process is cheaper, faster or more effective than removal of HAP precursors by other techniques such as physical or chemical cleaning. The value of the revenue stream is unknown for HAP precursor removal, but it is well known for sulfur. Emissions trading by two brokerage firms report a value of over \$110 per ton of sulfur dioxide traded as a "sulfur allowance" in early 1997. This results in a value of over \$220 per ton of sulfur that would be removed from coal prior to combustion, and is directly applied to the revenue stream of any process which removes sulfur. This value is directly measurable by the removal of pyritic sulfur in the biochemical processes under investigation.

The results of this project indicate that substantial percentages of certain HAP precursors can be removed from coal as a result of the activities of pyrite oxidizing microorganisms, and that these microorganisms may assist in subsequent removal of Hg during physical cleaning. Heaps or continuous vat processes are possible for the removal of HAP precursors from coarse coal (1/2") on a large scale. The slurry column reactor is a potential process option for fine coal. The phase 2 test work will determine the effectiveness of these competing designs for removal of HAP precursors from coal at the large laboratory-pilot scale. These data will permit an economic analysis of the processes, as well as an economic value for removal of HAP precursors. The economic value for sulfur removal is well known to industry from trading "sulfur allowances". The value of HAP precursor removal from coal is not known to industry at this time which may inhibit regulatory development. An extremely important result from the Phase 2 testing and economic model development will be the determination of the value of HAP precursors by the biochemical processes proposed.

The phase 1 test work on this project has been completed. The proposed research for phase 2 is to conduct large column tests (ton scale) and an additional slurry column test to provide the data required for a demonstration scale design and the subsequent economic analysis for a slurry column reactor process, a heap leach process, and a continuous vat leaching process. In addition, the effectiveness of Hg removal from coal by the physical separation component of the slurry column reactor will be determined to indicate the extent that microorganisms enhance the physical separation of Hg from coal. The outcome of the phase 2 test would show what the pilot plant for the microbiological removal of HAP precursors from coal will look like, how much it will cost to build and operate, and the economic value of HAP precursor removal.

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